

# An explanation of linear increases in gas concentration under closed chambers used to measure gas exchange between soil and the atmosphere

F. CONEN & K. A. SMITH

*Institute of Ecology and Resource Management, University of Edinburgh, West Mains Road, Edinburgh EH9 3JG, UK*

## Summary

Earlier models describing the accumulation of gases under closed chambers are based on the assumption of a constant concentration source that does not change during the time of chamber deployment. A new model is proposed which is based on the assumption of a constant production source, and takes into account possible changes in gas concentrations at the source during chamber deployment. Using  $\text{N}_2\text{O}$  as an example, simulations have been carried out for different source strength and depth, diffusivities and air porosities. The main finding was a chamber-induced increase in gas concentrations in the upper part of the soil profile, including the depth where the  $\text{N}_2\text{O}$  source is located. The increase started immediately after chamber closure. Nevertheless, fluxes calculated from increasing concentrations within the chamber's headspace were always less than those expected under undisturbed conditions, i.e. in the absence of a chamber. This was due to a proportion of the gas produced being stored within the soil profile while the chamber was in place. The discrepancy caused by this effect increased with increasing air-filled porosity and decreasing height of the chamber, and a procedure for correcting chamber flux measurements accordingly is proposed. The increase in soil gas concentrations after chamber closure was confirmed in a laboratory experiment.

## Introduction

By far the most widely used method of measuring fluxes of trace gases such as carbon dioxide, methane and nitrous oxide between soil and the atmosphere is based on the closed (or static) chamber. This is essentially a box covering a small area of the soil surface, within which the target gas accumulates during a period of closure (typically tens of minutes). The concentration increase is determined by a suitable method (e.g. infrared analysis for  $\text{CO}_2$ , gas chromatography for  $\text{CH}_4$  and  $\text{N}_2\text{O}$ ,  $\alpha$ -scintillation counting for radon), and the flux is calculated. Examples of typical systems are given in Matthias *et al.* (1980), Hutchinson & Mosier (1981) and Clayton *et al.* (1994).

Several models describing the accumulation of trace gases in these closed chambers include the assumption that there is a constant concentration of the target gas either at the interface between the soil and the atmosphere (Gao & Yates, 1998), or at a plane within the soil profile (Hutchinson & Mosier, 1981; Healy *et al.*, 1996) during the chamber closure period. However, Denmead (1979) had referred to a 'readjustment of the  $\text{N}_2\text{O}$  concentration in the soil air whenever the  $\text{N}_2\text{O}$

concentration in the chamber air changes from ambient'. These models conclude that the increase in concentration in the chamber leads to a decrease in the relative difference in concentration between the soil air near the surface and the atmosphere in the chamber, and therefore a decrease in the flux intensity with time should be observed. The corollary of this is that the graph of chamber concentration against time will be non-linear, and thus samples need to be taken at several time intervals during closure to calculate the flux.

By contrast, there is considerable direct experimental evidence from studies on a range of arable, grassland and forest soils of linear increases in gas concentration with time, after chamber closure. Matthias *et al.* (1980) found that this was the typical pattern observed for  $\text{N}_2\text{O}$  in arable soil in Iowa. Yamulki & Jarvis (1999) report linear increases in a study on grassland. The same was observed by Thomson (1998) in studies using monoliths of arable, grassland and forest soil. For radon ( $^{222}\text{Rn}$ ), accumulations in a chamber were found to be linear over 6 h (Dörr & Münnich, 1990).

The assumption in current models that the concentration of the target gas in the soil gas phase is constant at a certain depth for the limited time of chamber deployment has apparently never been tested in an experiment with natural soil. Nay *et al.* (1994) tested closed chambers with a model system consisting

of a chemical source supplying CO<sub>2</sub> into a footspace covered by polyurethane foam to simulate a porous soil layer. The CO<sub>2</sub> diffused through the foam into different types of chambers placed on the top surface. However, the authors regulated the CO<sub>2</sub> concentration in the footspace to keep it constant; thus the experiment could not show what happens when constant gas production occurs *in situ*.

We propose a different approach to the problem, which is based only on the assumption of a constant production rate of the target gas within the soil profile. This assumption is present also in previous models. However, we think it may not have been always built into the simulations. The main conclusion from our modelling has been compared with measurements made in a simple laboratory experiment, using a system comprising a soil monolith and flux chamber similar to that described by Thomson *et al.* (1997), but on a smaller scale.

## Materials and methods

### Model

The model we developed is based on the main assumption of a constant production of the target gas at a certain depth within the soil profile. We make further assumptions, which are unlikely to affect our model in principle, but which are a simplification of the complex spatial inhomogeneity of natural soils. Thus, we consider production and consumption to occur in the same location and be independent of the surrounding target gas concentration. This allows us to consider net production to be related to a certain depth only. Also, we assume the model soil to have a homogeneously distributed air-filled porosity (and thus the same diffusivity) at all depths, which is also constant throughout the period of interest. We assume the gas to mix readily in the atmosphere, or in the headspace of the chamber. As an example of a target gas we use N<sub>2</sub>O, which has a diffusivity in air of  $1.43 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$  (Pritchard & Currie, 1982). We calculated diffusivity in the soil in a way similar to that of Healy *et al.* (1996) as  $D_{\text{air}} \times \theta \times \theta^{1/3}$ , where  $\theta$  is the air-filled porosity of the soil. Our model treats the different soil depth as cells of 1 cm height. The lowest cell, at 30 cm depth, is assumed to be sealed at the bottom by an impermeable layer. The uppermost cell represents the atmosphere. This cell has an indefinite height when no chamber is in place, but it has the same height as the chamber when a situation with the closed chamber in place is simulated. Gas exchange occurs between the cells according to Fick's law of diffusion:

$$J = -D \frac{c_b - c_a}{d}, \quad (1)$$

where  $J$  is the flux,  $D$  is the diffusion coefficient,  $c_b$  is the gas concentration in cell  $b$ ,  $c_a$  is the gas concentration in cell  $a$ , and  $d$  is the vertical distance between the bottom of cell  $a$  and the bottom of cell  $b$ .

The gas concentration within a cell was calculated in 6-s time steps as follows:

$$c_i = c_{i-1} + \frac{J_{i-1}A}{V} + c_p, \quad (2)$$

where  $c_i$  is the concentration at time step  $i$ ,  $c_{i-1}$  is the concentration at the previous time step,  $c_p$  is the concentration increase due to gas production within the cell during one time step,  $J_{i-1}$  is the net flux resulting from gas diffusion into and out of the cell during the previous time step,  $A$  is the area of the horizontal cross-section of the cell, and  $V$  is the air volume of the cell.

We can define  $V$  as

$$V = \theta hA, \quad (3)$$

where  $\theta$  is the air-filled porosity, and  $h$  is the cell height.

Combining Equations (1), (2) and (3), we get

$$c_i = c_{i-1} + \frac{-D \frac{c_{i-1} - c_{(a)i-1}}{d} A + D \frac{c_{i-1} - c_{(c)i-1}}{d} A}{\theta hA} + c_p, \quad (4)$$

where  $c_{(a)i-1}$  is the concentration in neighbouring cell  $a$  at time step  $i-1$ , and  $c_{(c)i-1}$  is the concentration in neighbouring cell  $c$  at time step  $i-1$ .

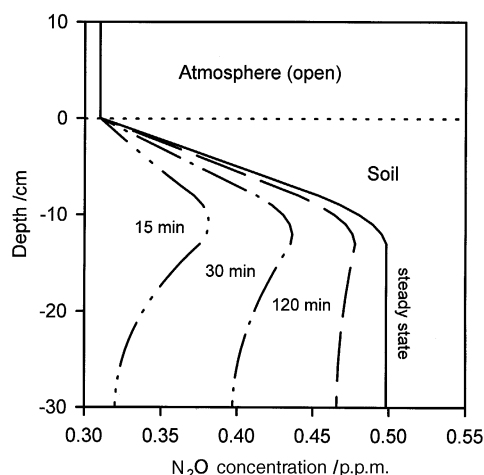
In this equation  $A$  cancels out, leaving us with

$$c_i = c_{i-1} + \frac{-D \frac{c_{i-1} - c_{(a)i-1}}{d} + D \frac{c_{i-1} - c_{(c)i-1}}{d}}{\theta h} + c_p. \quad (5)$$

To test our one-dimensional model we first simulated situations without a chamber and compared them prior to, and at, the steady state indicated by the general form of Equation (1). We then simulated concentration changes with closed chambers of different heights, and with different values for soil porosity and diffusivity. Initial concentrations were assigned to each cell as expected under steady-state conditions for the particular values of  $D$ ,  $J$  and source depth, and the changes over a 30-min interval were simulated. A linear regression was fitted to the chamber concentration over time and the flux into the chamber was calculated as the slope of this regression multiplied by the chamber height. This value was then compared with the total source strength, i.e. the flux under undisturbed conditions.

### Experiment

A soil core (24 cm diameter, 13 cm height) with associated plants, encased in a PVC cylinder, was taken from a grassland site at Glencorse Mains, 10 km south of Edinburgh, and brought to the laboratory on 16 February 1999. The soil had a clay loam texture (36% sand, 40% silt and 24% clay), an organic matter content of 5.5% and a bulk density of  $1.05 \text{ g cm}^{-3}$ . It was fertilized the following day with ammonium



**Figure 1** Development of an  $\text{N}_2\text{O}$  concentration profile in a soil of 20% air porosity, diffusivity of  $1.673 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ , and no initially enhanced  $\text{N}_2\text{O}$  concentrations. The soil surface is open to the atmosphere. The  $\text{N}_2\text{O}$  source forming this profile starts producing at a constant rate at time 0 and is of a total strength of  $12 \mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ . The theoretical steady-state concentrations (continuous line) are approached with declining speed. Profiles are shown for 15 min (line with two short dashes), 30 min (line with one short dash), and 120 min (line with no short dashes).

nitrate at a rate equivalent to  $100 \text{ kg N ha}^{-1}$  and subjected to three series of measurements on 25 February, 3 March and 8 March 1999. No water lost by evapotranspiration was added during this period, so as to get results for different soil moisture contents. The first series of measurements was made near field capacity.

The plastic cylinder enclosing the core was closed at the base with a cap of the same material, which had been fitted with a soil air sampler consisting of a perforated plastic tube (5 mm internal diameter, 0.45 m length), laid out in a circle and embedded in a 1-cm-high layer of medium sand. The sides of the core were sealed to the cylinder with wax to prevent gas movement. The 7 cm of the plastic cylinder protruding above the top of the core acted as a flux chamber that could be closed with a gas-tight plastic lid.

Gas samples from the space below the core, and from the space above the core, were taken at 20-min intervals and analysed on-line through 0.6-m-long, 4-mm-diameter Teflon<sup>®</sup> tubes connected to the automated gas chromatographic analysis system described by Arah *et al.* (1994). Ambient temperature during the measurements was constant at  $20^\circ\text{C}$ .

## Results

### Model

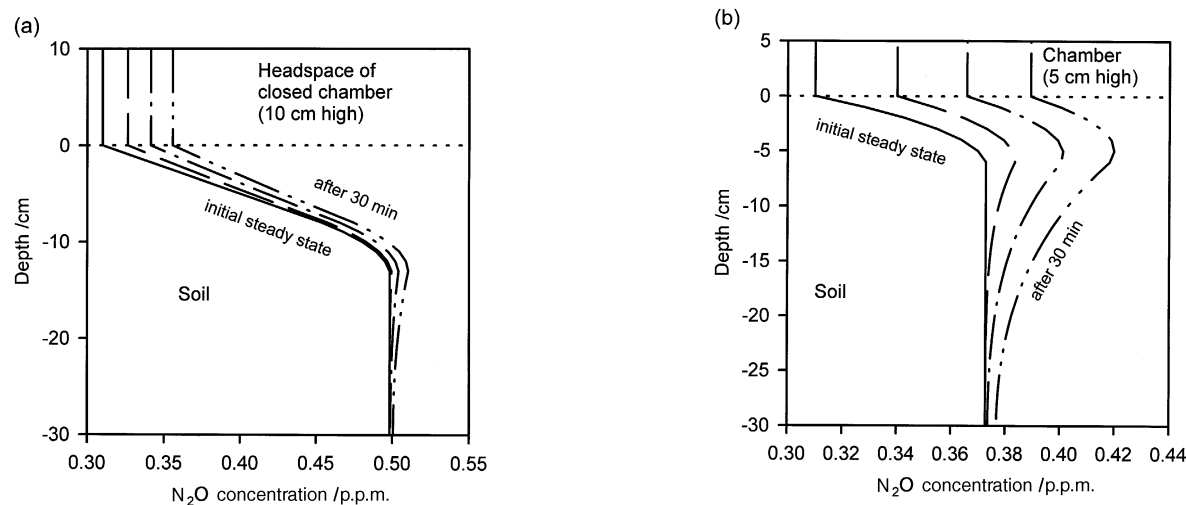
The model could reproduce the accumulation of a soil concentration profile when no chamber was in place. The

initial concentration in the soil profile was set equal to atmospheric concentration ( $0.31 \times 10^{-6} \text{ m}^3 \text{ m}^{-3}$ ). Soil porosity was set at 20% and  $D$  at  $1.673 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ . Concentrations increased quickly at the beginning, and the rate of increase declined as steady-state conditions were approached. This general pattern was independent of source strength. However, graphical illustration was clearer when weak sources were used in the simulation; the example shown in Figure 1 is for a constant source of  $12 \mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ , equally distributed between 8 and 13 cm depth.

Examples of simulations of concentration profiles under a closed chamber are shown in Figure 2. Soil conditions were the same as in the previous simulation. This time, however, the atmosphere above the soil was an enclosed headspace with a height of 10 cm (Figure 2a). Concentrations started to increase within the soil profile as soon as the chamber was closed. This increase began with the first 6-s time step and included the layer where the source was located. However, changes below the source became smaller with increasing depth. The increase in chamber concentration was almost linear ( $r^2 = 0.9994$ ). Nevertheless, the flux calculated from the concentration increase within the chamber was only 84% of the source strength. In certain circumstances, chamber concentrations were found to increase in excess of concentrations in the soil below the source. Such behaviour was found when the source was close to the surface, the soil was highly porous, and the chamber was shallow (5 cm). An example is shown in Figure 2(b). We ran many simulations and found that the proportion of the total flux that was measured was independent of the strength and depth of the source. It was also independent of whether the source was concentrated in a shallow layer, or whether it was evenly distributed within a layer several centimetres thick. Yet it depended on the air-filled porosity and associated diffusivity, as well as on the height of the chamber. Table 1 shows some results of our simulations. The proportion of the total production rate ( $J_m$ ) that was represented by the flux into the chamber was found to be between 72% for a 5-cm-high chamber on soil with an air-filled porosity of 20%, and 99% for a 30-cm-high chamber on a soil with an air-filled porosity of 5%. The concentration increase with time was always close to linear ( $r^2 > 0.99$ ) and became more and more so with increasing height of the chamber and decreasing soil porosity.

### Experiment

Emissions were largest, at  $388 \mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ , during the first series of measurements. The concentration in the chamber exceeded  $20 \times 10^{-6} \text{ m}^3 \text{ m}^{-3}$  at the end of the closure period (Figure 3a). Successive measurements as the soil dried out gave decreasing values of 67 and  $29 \mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ , respectively (Figure 3b,c). The concentration increase in the



**Figure 2** Development of N<sub>2</sub>O concentration profiles in a soil with 20% air porosity, diffusivity of  $1.673 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ , and initially steady-state concentrations at time 0 (continuous line). (a) The N<sub>2</sub>O source ( $12 \mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ ) is evenly distributed between 8 and 13 cm depth and the soil is covered with a 10-cm-high chamber. (b) The N<sub>2</sub>O source ( $12 \mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ ) is evenly distributed between 0 and 5 cm depth and the soil is covered with a 5-cm-high chamber. As concentrations increase within the headspace of the chamber, they also increase within the entire soil profile. Profiles are shown for 10 min (line with no short dashes), 20 min (line with one short dash), and 30 min (line with two short dashes) after chamber closure.

**Table 1** Linearity and proportion of total net N<sub>2</sub>O production ( $J_m$ ) measured with chambers of different height and on soils with different air porosity and a total depth of 30 cm

$\theta$ /%	$D$ $/\text{m}^2 \text{ s}^{-1} \times 10^{-6}$	Chamber height /cm	$r^2$ <sup>a</sup>	$J_m$ /%
20	1.673	5	0.9978	72
20	1.673	10	0.9994	84
20	1.673	20	0.9998	92
20	1.673	30	0.9999	94
10	0.664	5	0.9995	86
10	0.664	10	0.9999	93
10	0.664	20	1	96
10	0.664	30	1	97
5	0.264	5	0.9999	93
5	0.264	10	1	97
5	0.264	20	1	98
5	0.264	30	1	99

<sup>a</sup>Of linear regression; concentration over time.

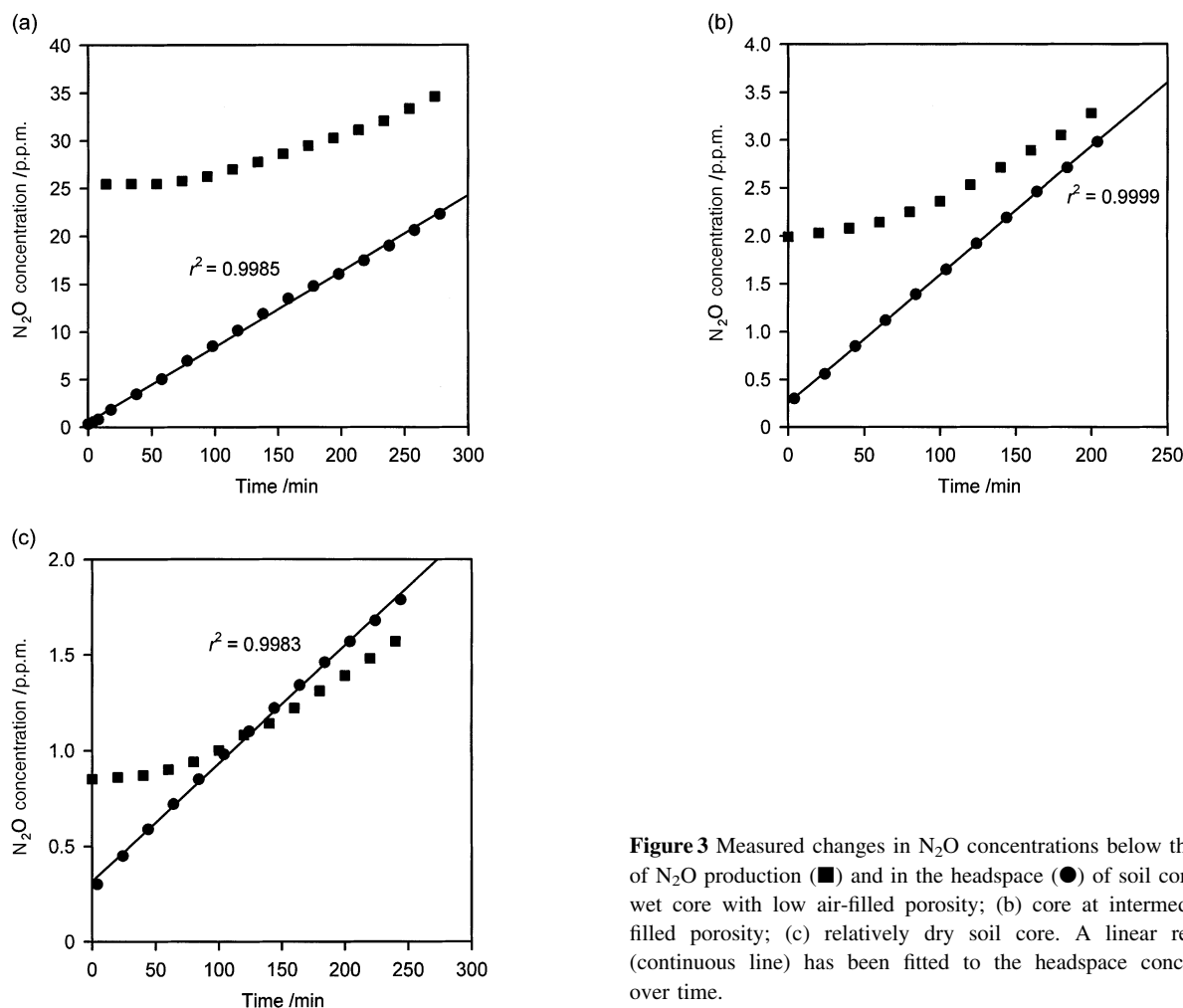
headspace was found, on all three occasions, to be virtually linear ( $r^2 > 0.9983$ ) over the entire period of closure, which ranged between 200 and 280 min. Also, increases in N<sub>2</sub>O concentrations were observed below the source of N<sub>2</sub>O production in the sand at the bottom of the core. These were less in amplitude and were delayed relative to the changes in the headspace concentration (Figure 3a,b,c). When the soil was relatively dry, the concentrations in the chamber increased

until they exceeded concentrations in the soil at the bottom of the core (Figure 3c).

**Discussion**

In this modelling approach we found that soil gas concentrations increased throughout the soil profile as soon as gas exchange between soil and the atmosphere was intercepted by a closed chamber. The increases were detectable even after the first time step of the simulation, 6 s after closure. The other main outcome of our model simulations was the increase in soil concentrations of our target gas at a depth greater than the source. This was supported by the experimental measurements. These results indicate that our approach offers advantages over the concept of a constant concentration, or a plane of constant concentration, of a target gas in the soil profile as assumed in previous models (Hutchinson & Mosier, 1981; Healy *et al.*, 1996; Gao & Yates, 1998).

We found that the concentration increases in the chamber headspace were either linear or very nearly so. Even the largest departure from linearity ( $r^2 = 0.9978$ ) found for the shallow chamber (5 cm) on the soil with 20% air-filled porosity was so small that it would be difficult to detect under field conditions by repeated sampling during the closure. Nevertheless, fluxes calculated from the increase in chamber concentrations were always less than the fluxes we expected under undisturbed conditions. This was because a proportion of the gas produced was stored within the soil profile rather than being emitted at the



**Figure 3** Measured changes in  $N_2O$  concentrations below the source of  $N_2O$  production (■) and in the headspace (●) of soil core for (a) wet core with low air-filled porosity; (b) core at intermediate air-filled porosity; (c) relatively dry soil core. A linear regression (continuous line) has been fitted to the headspace concentration over time.

surface, as we would expect under undisturbed equilibrium conditions between gas production and gas emission. The proportion of flux missed is directly related ( $r^2 = 0.99$ ) to the ratio of the total air volume within the soil profile underneath the chamber to the chamber's volume (Figure 4). This suggests that corrections could be made to measured fluxes, if the total volume of air in the soil is known. The underestimation of the flux can be calculated approximately from the regression in Figure 4 as

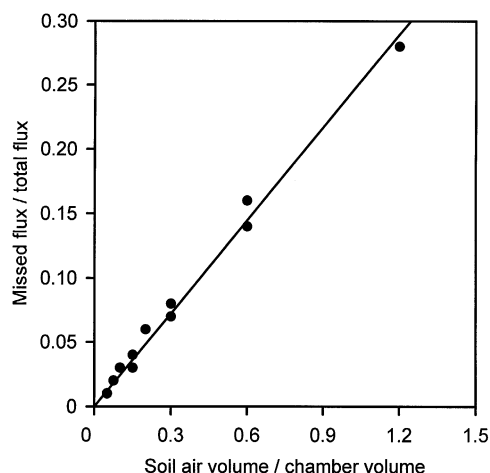
$$J_e = 0.24(V_s/V_c), \quad (6)$$

where  $J_e$  is the proportion of the flux that is missed,  $V_s$  is the total soil air volume underneath the chamber, and  $V_c$  is the chamber's volume.

The fact that we found chamber concentrations to increase in excess of concentrations in the soil at the bottom of our core (Figure 3c) suggests that the source of  $N_2O$  must have been close to the surface. This accords with the results of Luo *et al.* (1998), who found  $N_2O$  production in pasture soil to occur mainly in the top 5 cm. Since we did not determine the exact

depth of  $N_2O$  production within our soil core, it would need further assumptions to compare model predictions and experimental findings in detail. This would doubtless overstretch the outcome of our experiment, which was designed in such a way that it could be used only to test in principle the conclusions of our model.

In spite of our observations (and the others cited in the Introduction) of virtually linear increases in chamber concentration, non-linear accumulations have clearly been observed in some studies, and these need an alternative explanation. If the apparent emission rate of  $N_2O$  or  $CO_2$ , for example, increases with time after closure, this is most probably due to the soil's warming (Denmead, 1979) and a consequent increase in microbial activity. If the apparent rate decreases with time the possible explanations include soil cooling (Denmead, 1979), and increased diffusive escape from the chamber to the outside atmosphere, as the concentration difference increases. There are three likely pathways for such an escape: a leak in the chamber itself; an inadequate seal between the chamber wall and the soil; and diffusion through the topsoil and under the



**Figure 4** Relationship between underestimation of true flux and the ratio of total soil air volume to chamber volume, based on the results shown in Table 1. A linear regression has been fitted, with the intercept set at 0; the equation of the line is  $y=0.24x$ , where  $y$  is the proportion of the flux missed and  $x$  is the ratio of soil air volume to chamber volume ( $r^2$  for the regression is 0.9901).

chamber wall (which is commonly inserted to approximately 5 cm depth). The first two pathways should always be avoidable with sufficient care; the third is unlikely to be important in moist soils of medium to fine texture, but if the bottom of the chamber wall is within a dry sandy horizon of high diffusivity a significant loss could occur by diffusion through the soil. Anthony *et al.* (1995) reported that half of all chamber measurements in a large study on a 'very sandy soil' in Texas showed an emission rate that decreased in the second sampling interval after closure, compared with the first; loss through the soil could well have been responsible. Where such soil conditions prevail, it is desirable to make the chamber as large in area as possible, to maximize the ratio of emitting surface to wall circumference, and to maximize the height above the soil surface (consistent with analytical sensitivity), to avoid an excessive concentration difference between the chamber and the outside atmosphere. In any study it is prudent to carry out checks on linearity of gas accumulation in the local conditions before deciding whether single sampling at the end of a closure period will suffice, or whether multiple sampling times are needed within every closure period.

Finally, it should be noted that in relation to the effects of chamber closure on gas concentrations in the soil profile there is a major difference, which Gao & Yates (1998) ignored, between, on the one hand, those gases that are produced *in situ* (e.g.  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $^{222}\text{Rn}$ ) and, on the other, a gas such as the fumigant methyl bromide which is injected into the soil in a single operation. For the latter, the concentration may change little over a short period when emissions are being measured with a closed chamber, but as explained above this is not true for the other gases.

## Conclusions

There is a direct feedback effect of the headspace concentration in a closed chamber on the concentration at the source of gas production within the soil beneath it. This feedback is immediate and it is desirable to take account of it, rather than assume a constant soil gas concentration during the period of chamber deployment. The increase in soil gas concentration is also responsible for the departure from linearity of the flux increase under a closed chamber being much less than previously predicted. However, some proportion of the produced gas is stored within the soil profile while a closed chamber is in place. This leads to an underestimation of the real fluxes by the closed-chamber technique. One way to minimize this error is to maximize the chamber's height, provided there is sufficient analytical sensitivity to cope with the consequent dilution of the emitted gas. Another possibility is to estimate total volume of air in the soil underneath the chamber and to calculate the proportion of missed flux. Taking account of underestimation of fluxes is especially necessary on deep soils with a large air-filled porosity.

## Acknowledgements

We thank Dr Thomas Marik from the Max-Planck-Institut für Chemie in Mainz for his help in the modelling.

## References

- Anthony, W.H., Hutchinson, G.L. & Livingston, G.P. 1995. Chamber measurement of soil-atmosphere gas exchange: linear vs. diffusion-based flux models. *Soil Science Society of America Journal*, **59**, 1308–1310.
- Arah, J.R.M., Crichton, I.J., Smith, K.A., Clayton, H. & Skiba, U. 1994. Automated gas chromatographic analysis system for micro-meteorological measurements of trace gas fluxes. *Journal of Geophysical Research*, **99**, 16593–16598.
- Clayton, H., Arah, J.M.R. & Smith, K.A. 1994. Measurement of nitrous emissions from fertilized grassland using closed chambers. *Journal of Geophysical Research*, **99**, 16599–16607.
- Denmead, O.T. 1979. Chamber systems for measuring nitrous oxide emissions from soils in the field. *Soil Science Society of America Journal*, **43**, 89–95.
- Dörr, H. & Münnich, K.O. 1990.  $^{222}\text{Rn}$  flux and soil air concentration profiles in West-Germany: soil  $^{222}\text{Rn}$  as tracer for gas transport in the unsaturated soil zone. *Tellus*, **42B**, 20–28.
- Gao, F. & Yates, S.R. 1998. Simulation of enclosure-based methods for measuring gas emissions from the soil to the atmosphere. *Journal of Geophysical Research*, **103**, 26127–26136.
- Healy, R.W., Striegl, R.G., Russell, T.F., Hutchinson, G.L. & Livingston, G.P. 1996. Numerical evaluation of static-chamber measurements of soil-atmosphere gas exchange: identification of physical processes. *Soil Science Society of America Journal*, **60**, 740–747.
- Hutchinson, G.L. & Mosier, A.R. 1981. Improved soil cover method

- for field measurements of nitrous oxide fluxes. *Soil Science Society of America Journal*, **45**, 311–316.
- Luo, J., Tillman, R.W., White, R.E. & Ball, P.R. 1998. Variation in denitrification activity with soil depth under pasture. *Soil Biology and Biochemistry*, **30**, 897–903.
- Matthias, A.D., Blackmer, A.M. & Bremner, J.M. 1980. A simple chamber technique for field measurement of emissions of nitrous oxide from soils. *Journal of Environmental Quality*, **9**, 251–256.
- Nay, S.M., Mattson, K.G. & Bormann, B.T. 1994. Biases of chamber methods for measuring soil CO<sub>2</sub> efflux demonstrated with a laboratory apparatus. *Ecology*, **75**, 2460–2463.
- Pritchard, D.T. & Currie, J.A. 1982. Diffusion coefficients of carbon dioxide, nitrous oxide, ethylene and ethane in air and their measurement. *Journal of Soil Science*, **33**, 175–184.
- Thomson, P.E. 1998. *Factors controlling N<sub>2</sub>O emissions from soils: a study using a novel soil monolith/flux chamber system*. PhD thesis, University of Edinburgh.
- Thomson, P.E., Parker, J.P., Arah, J.R.M., Clayton, H. & Smith, K.A. 1997. Automated soil monolith–flux chamber system for the study of trace gas fluxes. *Soil Science Society of America Journal*, **61**, 1323–1330.
- Yamulki, S. & Jarvis, S.C. 1999. Automated chamber technique for gaseous flux measurements: evaluation of a photoacoustic infrared spectrometer–trace gas analyzer. *Journal of Geophysical Research*, **104**, 5463–5469.